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<p>(21) International Application Number: PCT/US97/08862 (22) International Filing Date: 22 May 1997 (22.05.97) (71) Applicant (for all designated States except US): PHILLIPS PETROLEUM COMPANY [US/US]; P.O. Box 2443, Bartlesville, OK 74005 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PALACKAL, Syriac, Joseph [IN/US]; 2501 Dorchester, Bartlesville, OK 74006 (US). WELCH, Melvin, Bruce [US/US]; 4750 Lewis Drive, Bartlesville, OK 74006 (US). STOUFFER, Carlton, E. [US/US]; 1406 Quiet Green Court, Houston, TX 77062 (US). NORWOOD, Donald, Dwight [US/US]; 3011 Sheri- dan Road, Bartlesville, OK 74006 (US). (74) Agents: DOLLAR, Beverly, M. et al.; Richmond, Hitchcock, Fish &amp; Dollar, P.O. Box 2443, Bartlesville, OK 74005 (US).</p>	<p>(81) Designated States: AU, BR, CA, CN, CZ, HU, IL, JP, KR, MX, NO, PL, SG, TR, US, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i></p>	
<p>(54) Title: METHOD FOR MAKING AND USING A PREPOLYMERIZED OLEFIN POLYMERIZATION CATALYST (57) Abstract A catalyst is prepared by creating a catalyst solution by combining an aluminoxane with a group 4-6 metallocene having a substituent which has olefinic unsaturation in a suitable ligand to form a liquid catalyst, conducting prepolymerization of an olefin on the liquid catalyst, and separating the resulting solid metallocene-containing catalyst from the reaction mixture, wherein the prepolymerization is conducted below 15 °C at a constant temperature and/or the resulting solid metallocene-containing catalyst is combined with a particulate polyethylene. Polymerization of olefins using the inventive solid catalyst is also disclosed.</p>		

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METHOD FOR MAKING AND USING A PREPOLYMERIZED  
OLEFIN POLYMERIZATION CATALYST

Field of the Invention

This invention relates to a new type of solid particulate metallocene catalyst system useful for the polymerization and/or copolymerization of olefins. The invention is also related to a process for conducting polymerization of olefins using the inventive solid metallocene catalyst system.

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Background of the Invention

The term "Metallocene" as used herein refers to a derivative of cyclopentadienylidene which is a metal derivative containing at least one cyclopentadienyl component which is bonded to a transition metal. The transition metal is selected from Groups IVB, VB, and VIB, preferably IVB and VIB. Examples include titanium, zirconium, hafnium, chromium, and vanadium. A number of metallocenes have been found to be useful for the polymerization of olefins. Generally, the more preferred catalysts are metallocenes of Zr, Hf, or Ti.

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Generally, in order to obtain the highest activity from metallocene catalysts, it has been necessary to use them with an organoaluminum cocatalyst, such as methylaluminum. This resulting catalyst system is generally referred to as a homogenous catalyst system since at least part of the metallocene or the organoaluminum is in solution in the polymerization media. These homogenous catalyst systems have the disadvantage that when they are used under slurry polymerization conditions, they produce polymer which sticks to reactor walls during the polymerization process and/or polymer having small particle size and low bulk density which limits the commercial utility.

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Some attempts to overcome the disadvantages of the homogenous metallocene catalyst systems are disclosed in U.S. Patents 5,240,894, 4,871,705; and 5,106,804. Typically, these procedures have involved the prepolymerization of the metallocene aluminum catalyst system either in the presence of or in the absence of a support. An evaluation of these techniques has revealed that there is still room for improvement, particularly when the catalyst is one which is to be used in a slurry type polymerization

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where the object is to produce a slurry of insoluble particles of the end product polymer rather than a solution of polymer which could result in fouling of the reactor. In the operation of a slurry polymerization in a continuous loop reactor it is extremely important for efficient operations to limit polymer fouling of the internal surfaces of the reactor. The  
5 term "fouling" as used herein refers to polymer buildup on the surfaces inside the reactor.

U.S. Patent No. 5,498,581 discloses a new type of prepolymerized metallocene catalyst system that can be used in slurry polymerization with little if any fouling. The patent teaches carrying out the prepolymerization at temperatures in the range of about -15°C to about +110°C or more preferably about 10°C to about 30°C. One aspect of the present  
10 invention is based upon the discovery that if one uses prepolymerization temperatures of less than 10°C there is a reduction in the amount of polymer fines produced when the catalyst system is employed in slurry polymerization. Another aspect of the present invention involves employing particulate polyethylene as a feeding aid for the prepolymerized catalyst system.

15 An object of the present invention is to provide improvements to the solid metallocene catalyst systems of the type disclosed in U.S. Patent No. 5,409,581, the disclosure of which is incorporated herein by reference. In accordance with another aspect of the present invention, there is provided a method for polymerizing olefins using the new improved version of such prepolymerized metallocene.

20 Summary of the Invention

In accordance with the present invention, a solid particulate metallocene-containing catalyst system is produced by (a) combining an cocatalyst and at least one metallocene having at least one cyclopentadienyl-type ligand having at least one olefinic unsaturated substituent in a liquid to form a liquid catalyst system, (b) conducting  
25 prepolymerization of at least one olefin in the presence of said liquid catalyst system to produce a prepolymerized solid catalyst, and (c) separating the resulting solid from the liquid and the components dissolved in the liquid, said solid being the solid particulate metallocene catalyst system, said invention being further characterized by at least one of the following improvements, namely,

(1) conducting the prepolymerization by beginning at a temperature of less than 10°C and maintaining the prepolymerization temperature within the range of 3°C to 5°C of the beginning temperature, or

(2) combining the prepolymerized solid catalyst with particulate polyethylene.

5 In accordance with another aspect of the present invention, the resulting inventive solid particulate metallocene-containing catalyst system is employed in the polymerization of an olefin by contacting the olefin with the inventive solid particulate metallocene-containing catalyst system under suitable reaction conditions.

#### Detailed Description of the Invention

10 It is contemplated that the cocatalyst can be selected from any of the compounds found useful as activators for metallocenes. Some typical examples include organometallic compounds of Group IA, IIA, and IIB of the Periodic Table. Specific examples include organometallic halide compounds, organometallic hydride compounds, and metal halides. Some specific examples include triethylaluminum, triisobutylaluminum, 15 diethylaluminum chloride, diethylaluminum hydrides, and alkyl aluminoxanes. Also included are the fluorophenyl boron compounds that have been found suitable as cocatalysts for metallocenes. One specific example is triphenyl carbenium tetrakis (pentafluorophenyl) boronate as disclosed in U.S. Patent 5,155,080.

20 The phrase "liquid catalyst system" as used herein refers to the combination of the cocatalyst, the metallocene, and the liquid, irrespective of whether the aluminoxane and/or the metallocene are dissolved in the liquid.

25 A wide range of metallocenes are considered to be applicable to the present process. The essential feature is that the metallocene be one wherein at least one cyclopentadienyl-type ligand has a substituent having a polymerizable olefinic group. Some examples of such olefin-containing metallocenes are disclosed in U.S. Patent 5,169,818 and published European Application No. 574,370. The invention is considered applicable to both bridged and unbridged metallocenes. The unbridged metallocenes can even include bridged ligands which contain two cyclopentadienyl-type radicals connected by a suitable bridging structure but wherein only one of the cyclopentadienyl-type radicals of that ligand is bonded

to the transition metal. Alternatively the olefinic substituent can be on the bridge connecting the two cyclopentadienyl-type groups.

The metallocenes of the type contemplated as useful for the present invention include those represented by the formula  $R_x(Z)(Z)MeQ_k$  wherein each Z bound to Me and  
 5 is the same or different and is a cyclopentadienyl-type ligand selected from substituted or unsubstituted cyclopentadienyl, indenyl, tetrahydroindenyl, octahydrofluorenyl, and fluorenyl ligands; R is a structural bridge linking the Z's and Me is a metal selected from the group consisting of IVB, VB, and VIB metals of the periodic table, each Q is the same or different and is selected from the group consisting of hydrogen, halogens, and organo  
 10 radicals; x is 1 or 0; k is a number sufficient to fill out the remaining balances of Me; further characterized by the fact that at least one Z has at least one olefinically unsaturated substituent attached. In bridged metallocenes this olefinically unsaturated substituent can be a branch on the bridging unit or on one or both of the cyclopentadienyl-type groups of the bridged ligands, or all three. Some currently preferred units for the bridge R include divalent  
 15 alkylidenes having one to four carbons, not counting the carbons of an olefinically branched substituent of the bridge.

A particularly preferred type of bridged metallocene includes those in which the olefinically unsaturated substituent has the formula



wherein R'' is a hydrocarbyl diradical having 1 to 20 carbon atoms; more preferably 2 to 10; n is 1 or 0, and each R' is individually selected from the group consisting of organo radicals having 1 to 10 carbon atoms and hydrogen. Most preferably R'' has at least two carbons in  
 25 its main alkylene chain, i.e. it is a divalent ethylene radical or a higher homolog thereof.

Some olefinic branched bridged ligands useful for making metallocenes suitable for the present invention can be prepared by reacting a dihalo olefinic compound

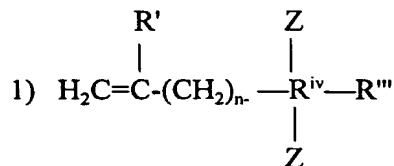
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with an alkali metal salt of a suitable cyclopentadiene-type compound to produce a compound of the formula Z-R-Z where R is a bridge having olefinic unsaturation and wherein each Z is the same or alternatively to produce a compound of the formula Z-R-X wherein X is a halogen and then reacting that compound with an alkali metal salt of another  
5 different cyclopentadiene-type compound to produce a compound of the formula Z-R-Z wherein the two Z's differ. Such reactions can be carried out using conditions of the type disclosed in U.S. Patent 5,191,132.

An alternate technique for forming an olefinic branched bridged ligand involves reacting a carbonyl compound having olefinic unsaturation with a  
10 cyclopentadiene-type compound in the presence of a base and methanol to yield an alkenyl fulvene which is then reacted with an alkali metal salt of a cyclopentadiene-type compound, such as, for example, fluorene, to yield the unsaturated-branched-bridged ligand containing two cyclopentadienyl-type groups, i.e. fluorenyl and cyclopentadienyl. For example, one could react 5-hexene-2-one with cyclopentadiene using a procedure like that disclosed by  
15 Stone et al in J. Org. Chem., 49, 1849 (1984) to yield 6-(but-3-enyl)-6-methylfulvene which could then be reacted with fluorenyllithium and subsequently hydrolyzed to yield 5-cyclopentadienyl-5-(9-fluorenyl)-1-hexene, also sometimes referred to as 1-(9-fluorenyl)-1-(cyclopentadienyl)-1-(methyl)-1-(but-3-enyl) methane.

The present invention thus envisions using bridged metallocenes prepared from  
20 vinyl terminated branched bridged ligands of the formula

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wherein n is a number typically in the range of about 0 to 20; more preferably 2-10; R<sup>iv</sup> is Si, Ge, C, or Sn; R<sup>iii</sup> and R' are each individually selected from hydrogen, or organo groups having 1 to 10 carbons. Currently preferred R' and R<sup>iii</sup> components are hydrogen or alkyl groups typically having 1 to 10 carbon atoms, or aryl groups typically having 6 to 10 carbon atoms. Z is a cyclopentadienyl-type radical as described earlier.

10

The metallocenes of such olefinically unsaturated branched-bridged ligands can be prepared by reacting the olefinically branched-bridged bis(cyclopentadienyl-type) ligand with an alkali metal alkyl to produce a divalent ligand salt that is then reacted with the transition metal compound to yield the metallocene, using the techniques generally known in the art for forming such metallocenes. See, for example, the technique disclosed in European Published Application 524,624, the disclosure of which is incorporated herein by reference.

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Some typical examples of some metallocenes containing a substituent having olefinic unsaturation include 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium dichloride, bis(9-fluorenyl)(methyl)(vinyl)silane zirconium dichloride, bis(9-fluorenyl)(methyl)(prop-2-enyl)silane zirconium dichloride, bis(9-fluorenyl)(methyl)(but-3-enyl)silane zirconium dichloride, bis(9-fluorenyl)(methyl)(hex-5-enyl)silane zirconium dichloride, bis(9-fluorenyl)(methyl)(oct-7-enyl)silane zirconium dichloride,

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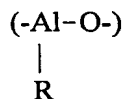


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(cyclopentadienyl)(1-allylindenyl) zirconium dichloride, bis(1-allylindenyl) zirconium dichloride, (9-(prop-2-enyl) fluorenyl) (cyclopentadienyl) zirconium dichloride, (9-(prop-2-enyl) fluorenyl)(pentamethylcyclopentadienyl) zirconium dichloride, bis(9-(prop-2-enyl)fluorenyl) zirconium dichloride, (9-(cyclopent-2-enyl) fluorenyl) (cyclopentadienyl) zirconium dichloride, bis(9-(cyclopent-2-enyl) (fluorenyl) zirconium dichloride, 5-(2-methylcyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium dichloride, 5-(fluorenyl)-5-(cyclopentadienyl)-1-hexene hafnium dichloride, (9-fluorenyl)(3-allyl-1-indenyl)dimethylsilane zirconium dichloride, 1-(2,7-di(alpha-methylvinyl)(9-fluorenyl))-1-(cyclopentadienyl)-1,1-dimethylmethane zirconium dichloride, 10 1-(2,7-di(cyclohex-1-enyl)(9-fluorenyl))-1-(cyclopentadienyl)-1,1-methane zirconium dichloride, 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dichloride, and the like.

These various metallocenes can be prepared by reacting the necessary cyclopentadienyl-type alkali metal salt with a transition metal compound. Some examples of such reactions are disclosed in the aforementioned published EPC application no. 524,624.

15 The organo aluminoxane component used in preparing the inventive solid catalyst system is an oligomeric aluminum compound having repeating units of the formula



20 Some examples are often represented by the general formula  $(\text{R}-\text{Al}-\text{O})_n$  or  $\text{R}(\text{R}-\text{Al}-\text{O})_n\text{AlR}^2$ . In the general alumoxane formula R is a  $\text{C}_1$ - $\text{C}_5$  alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "n" is an integer from 1 to about 50. Most preferably, R is methyl and "n" is at least 4. Aluminoxanes can be prepared by various procedures known in the art.

For example, an aluminum alkyl may be treated with water dissolved in an inert organic solvent, or it may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an aluminoxane. Generally the reaction of an aluminum alkyl with a limited amount of water is postulated to yield a mixture of the linear and cyclic species of the aluminoxane.

In the first step of the present invention, the metallocene and aluminoxane are combined in the presence of a suitable liquid to form a liquid catalyst system. It is preferred that the liquid catalyst system be prepared using an organic liquid in which the aluminoxane is at least partially soluble. The currently preferred liquids are hydrocarbons such as hexane or toluene. Typically some aromatic liquid solvent is employed. Examples include benzene, toluene, ethylbenzene, diethylbenzene, and the like. The amount of liquid to be employed is not particularly critical. Nevertheless, the amount should preferably be such as to dissolve the product of the reaction between the metallocene and the aluminoxane, provide desirable polymerization viscosity for the prepolymerization, and to permit good mixing. The temperature is preferably kept below that which would cause the metallocene to decompose. Typically the temperature would be in the range of  $-50^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . Preferably, the metallocene, the aluminoxane, and the liquid diluent are combined at room temperature, i.e. around  $10$  to  $30^{\circ}\text{C}$ . The reaction between the aluminoxane and the metallocene is relatively rapid. The reaction rate can vary depending upon the ligands of the metallocene. It is generally desired that they be contacted for at least about a minute to about 1 hour.

It is within the scope of the invention to form the liquid catalyst system in the presence of a particulate solid. Any number of particulate solids can be employed as the

particulate solid. Typically the support can be any organic or inorganic solid that does not interfere with the desired end result. Examples include porous supports such as talc, inorganic oxides, and resinous support materials such as particulate polyolefins. Examples of inorganic oxide materials include Groups II, III, IV or V metal oxides such as silica, alumina, silica-alumina, and mixtures thereof. Other examples of inorganic oxides are magnesia, titania, zirconia, and the like. Other suitable support materials which can be employed include such as, magnesium dichloride, and finely divided polyolefins, such as polyethylene. It is within the scope of the present invention to use a mixture of one or more of the particulate solids.

10 It is generally desirable for the solid to be thoroughly dehydrated prior to use, preferably it is dehydrated so as to contain less than 1 wt% loss on ignition. Thermal dehydration treatment may be carried out in vacuum or while purging with a dry inert gas such as nitrogen at a temperature of about 20°C to about 1000°C, and preferably, from about 300°C to about 800°C. Pressure considerations are not critical. The duration of thermal treatment can be from about 1 to about 24 hours. However, shorter or longer times can be employed provided equilibrium is established with the surface hydroxyl groups.

Dehydration can also be accomplished by subjecting the solid to a chemical treatment in order to remove water and reduce the concentration of surface hydroxyl groups. Chemical treatment is generally capable of converting all water and hydroxyl groups in the oxide surface to relatively inert species. Useful chemical agents are for example, trimethylaluminum, ethyl magnesium chloride, chlorosilanes such as  $\text{SiCl}_4$ , disilazane, trimethylchlorosilane, dimethylaminotrimethylsilane and the like.

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The chemical dehydration can be accomplished by slurring the inorganic particulate material such as, for example silica, in an inert low boiling hydrocarbon, such as for example, hexane or toluene. During the chemical dehydration treatment, the silica should be maintained in a moisture and oxygen free atmosphere. To the silica slurry is then added  
5 an inert hydrocarbon solution of the chemical dehydrating agent, such as, for example dichlorodimethylsilane. The solution is added slowly to the slurry. The temperature ranges during chemical dehydration reaction can be from about 20°C to about 120°C, however, higher and lower temperatures can be employed. Preferably, the temperature will be about 50°C to about 100°C. The chemical dehydration procedure should be allowed to proceed  
10 until all the substantially reactive groups are removed from the particulate support material as indicated by cessation of gas evolution. Normally, the chemical dehydration reaction will be allowed to proceed from about 30 minutes to about 16 hours, preferably, 1 to 5 hours. Upon completion of the chemical dehydration, the solid particulate material may be filtered under a nitrogen atmosphere and washed one or more times with a dry, oxygen free inert  
15 solvent. The wash solvents as well as the diluents employed to form the slurry and the solution of chemical dehydrating agent, can be any suitable inert hydrocarbon. Illustrative of such hydrocarbons are pentane, heptane, hexane, toluene, isopentane and the like.

Another chemical treatment that can be used on solid inorganic oxides such as silica involves reduction by contacting the solid with carbon monoxide at an elevated  
20 temperature sufficient to convert substantially all the water and hydroxyl groups to relatively inactive species.

The specific particle size of the support or inorganic oxide, surface area, pore

volume, and number of hydroxyl groups is not considered critical to its utility in the practice of this invention. However, such characteristics often determine the amount of support to be employed in preparing the catalyst compositions, as well as affecting the particle morphology of polymers formed. The characteristics of the carrier or support must therefore  
5 be taken into consideration in choosing the same for use in the particular invention.

It is also within the scope of the present invention to add such a particulate solid to the liquid catalyst system after it has been formed and to carry out the prepolymerization in the presence of that solid.

The amount of aluminoxane and metallocene used in forming the liquid  
10 catalyst system for the prepolymerization can vary over a wide range. Typically, however, the molar ratio of aluminum in the aluminoxane to transition metal of the metallocene is in the range of about 1:1 to about 20,000:1, more preferably, a molar ratio of about 10:1 to about 2000:1 is used. If a particulate solid, i.e. silica, is used generally it is used in an amount such that the weight ratio of the metallocene to the particulate solid is in the range  
15 of about 0.00001/1 to 1/1, more preferably 0.0005/1 to 0.2/1.

The prepolymerization is conducted in the liquid catalyst system, which can be a solution, a slurry, or a gel in a liquid. A wide range of olefins can be used for the prepolymerization. Typically, the prepolymerization will be conducted using an olefin, preferably selected from ethylene and non-aromatic alpha-olefins, and as propylene. It is  
20 within the scope of the invention to use a mixture of olefins, for example, ethylene and a higher alpha olefin can be used for the prepolymerization. The use of, a higher alpha olefin, such as 1-butene, with ethylene is believed to increase the amount of copolymerization

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occurring between the olefin monomer and the olefinically unsaturated portion of the metallocene. The prepolymerization can be carried out in one or more prepolymerization steps.

The prepolymerization steps should be conducted under relatively mild conditions. Typically, this would involve using low pressures of the olefin and relatively low temperatures designed to prevent site decomposition resulting from high concentrations of localized heat. The prepolymerization can be conducted over a wide range of temperatures, typically the temperatures would be in the range of about  $-15^{\circ}\text{C}$  to about  $+110^{\circ}\text{C}$ . In accordance with a preferred embodiment of the present invention the prepolymerization is begun at a temperature of less than  $10^{\circ}\text{C}$  and maintained within about  $3^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  throughout the prepolymerization, preferably the beginning temperature for the prepolymerization would be conducted at a temperature in the range of about  $-15^{\circ}\text{C}$  to about  $+9^{\circ}\text{C}$ , still more preferably in the range of about  $-10^{\circ}\text{C}$  to about  $+5^{\circ}\text{C}$ , and still more preferably about  $0^{\circ}\text{C}$ .

The amount of prepolymer can be varied but typically would be in the range of from about 1 to about 95 wt % of the resulting prepolymerized solid catalyst system, more preferably about 5 to 80 wt %. It is generally desirable to carry out the prepolymerization to at least a point where substantially all of the metallocene is in the solid rather than in the liquid since that maximizes the use of the metallocene. When the prepolymerization is conducted at the lower temperatures it can take longer to achieve the desired level of prepolymer.

After the prepolymerization, the resulting solid prepolymerized catalyst is

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separated from the liquid of the reaction mixture. Various techniques known in the art can be used for carrying out this step. For example, the material could be separated by filtration, decantation, or by vacuum evaporation. It is currently preferred, however, not to rely upon vacuum evaporation since it is considered desirable to remove substantially all of the soluble components in the liquid reaction product of the prepolymerization from the resulting solid prepolymerized catalyst before it is stored or used for subsequent polymerization. After separating the solid from the liquid, the resulting solid is preferably washed with a hydrocarbon and then dried using high vacuum to remove substantially all the liquids and other volatile components that might still be associated with the solid. The vacuum drying is preferably carried out under relatively mild conditions, i.e. temperatures below 100°C. More typically the prepolymerized solid is dried by subjection to a high vacuum at a temperature of about 30°C to about 50°C until a substantially constant weight is achieved. A preferred technique employs at least one initial wash with an aromatic hydrocarbon, such as toluene, followed by a wash with a paraffinic hydrocarbon, such as hexane, and then vacuum drying.

It is within the scope of the present invention to contact the prepolymerization reaction mixture product with a liquid in which the prepolymer is sparingly soluble, i.e. a countersolvent for the prepolymer, to help cause soluble prepolymer to precipitate from the solution. Such a liquid is also useful for the subsequent washing of the prepolymerized solid.

It is also within the scope of the present invention to add a particulate solid of the type aforementioned after the prepolymerization. Thus one can add the solid to the liquid

prepolymerization product before the countersolvent is added. In this manner soluble prepolymer tends to precipitate onto the surface of the solid to aid in the recovery of the filtrate in a particulate form and to prevent agglomeration during drying. The liquid mixture resulting from the prepolymerization or the inventive solid prepolymerized catalyst can be  
5 subjected to sonification to help break up particles if desired.

Further, if desired the recovered solid prepolymerized catalyst system can be screened to give particles having sizes that meet the particular needs for a particular type of polymerization. It is generally desirable to remove particles that are too large to be readily handled in the polymerization process.

10 Another option is to combine the recovered inventive solid prepolymerized catalyst system with an inert hydrocarbon, such as one of the type used as a wash liquid, and then to remove that liquid using a vacuum. In such a process it is sometimes desirable to subject the resulting mixture to sonification before stripping off the liquid.

The resulting solid prepolymerized metallocene-containing catalyst system is  
15 useful for the polymerization of olefins. Generally, it is not necessary to add any additional aluminoxane to this catalyst system. In some cases it may be found desirable to employ small amounts of an organoaluminum compound as a scavenger for poisons. The term organoaluminum compounds include compounds such as triethylaluminum, trimethylaluminum, diethylaluminum chloride, ethylaluminum dichloride, ethylaluminum  
20 sesquichloride, and the like. Trialkylaluminum compounds are currently preferred. Also in some applications it may be desirable to employ small amounts of antistatic agents which assist in preventing the agglomeration of polymer particles during polymerization.



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Still further, when the inventive catalyst system is added to a reactor as a slurry in a liquid, it is sometimes desirable to add a particulate dried solid as a flow aid for the slurry. Preferably the solid has been dried using one of the methods described earlier. Inorganic oxides such as silica are an example. One example is fumed silica such as that  
5 sold under the tradename Cab-o-sil. Generally the fumed silica is dried using heat and trimethylaluminum. In accordance with a preferred embodiment of the invention polyethylene fluff is used as the particulate solid flow aid. It has been found that if polyethylene fluff is used it is possible to carry out the polymerizations in a continuous loop slurry process using less antistatic agent than would generally be used if fumed silica were  
10 used. The use of the particulate diluents is particularly useful in those polymerization systems where catalyst is allowed to accumulate in a vessel, often referred to in the art as a mudpot, and then introduced into the polymerization vessel via a check valve capable of delivering specific amounts of the slurry. Some examples of such catalyst charging devices are disclosed in U.S. Patents 4,767,028, 5,098,667, and 5,404,219 and in various publications  
15 mentioned in those patents. The particulate diluent serves to aid in the feeding of the catalyst through the check value and helps to minimize wide variations in the amount of the catalyst being charged to the polymerization reactor.

The particulate polyethylene used as the feed aid is preferably a polyethylene fluff. The size of the polyethylene particles can vary over a wide range but typically it is  
20 preferred that the particles are predominately of sizes in the range of about 1 mm to about 0.074 mm. More preferably the predominate particles are those having sizes in the range of 0.5 mm to 0.15 mm. The amount of polyethylene fluff combined with the catalyst can vary

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over a wide range; however, for best feeding results it has been found desirable to employ about 2 parts by weight of the particulate polyethylene per part by weight of the prepolymerized catalyst system. The mixture of the catalyst and the polyethylene fluff can be used in either the dry form, wetted with a suitable organic liquid, or in the form of a slurry in a suitable organic liquid. Typically, aliphatic hydrocarbons are used as the liquid, typical examples including hexane and isobutane. The currently preferred types of polyethylene fluff are those made using a high activity titanium-containing catalyst such as those disclosed in U.S. 4,326,988.

The inventive solid prepolymerized catalyst system is particularly useful for the polymerization of alpha-olefins having 2 to 10 carbon atoms. Examples of such olefins include ethylene, propylene, butene-1, pentene-1, 3-methylbutene-1, hexene-1, 4-methylpentene-1, 3-methylpentene-1, heptene-1, octene-1, decene-1, 4,4-dimethyl-1-pentene, 4,4-diethyl-1-hexene, 3,4-dimethyl-1-hexene, and the like and mixtures thereof. The catalysts are also useful for preparing copolymers of ethylene and propylene and copolymers of ethylene or propylene and a higher molecular weight olefin.

The polymerizations can be carried out under a wide range of conditions depending upon the particular metallocene employed and the particular results desired. Although the inventive catalyst system is a solid, it is considered that it is useful for polymerization conducted under solution, slurry, or gas phase reaction conditions.

When the polymerizations are carried out in the presence of liquid diluents obviously it is important to use diluents which do not have an adverse effect upon the catalyst system. Typical liquid diluents include propane, butane, isobutane, pentane, hexane,

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heptane, octane, cyclohexane, methylcyclohexane, toluene, xylene, and the like. Typically the polymerization temperature can vary over a wide range, temperatures typically would be in a range of about  $-60^{\circ}\text{C}$  to about  $300^{\circ}\text{C}$ , more preferably in the range of about  $20^{\circ}\text{C}$  to about  $160^{\circ}\text{C}$ . Typically the pressure of the polymerization would be in the range of from about 1 to about 500 atmospheres or even greater. The inventive catalyst system is particularly useful for polymerizations carried out under particle form, i.e., slurry-type polymerization conditions.

The polymers produced with this invention have a wide range of uses that will be apparent to those skilled in the art from the physical properties of the respective polymers.

Applications such as molding, films, adhesives, and the like are indicated.

A further understanding of the present invention, its various aspects, objects and advantages will be provided by the following examples.

#### Example I

In this synthesis 20.6 mL of cyclopentadiene and 11.7 mL of 5-hexene-2-one were dissolved in 100 mL of methanol. While cooling in ice 12.4 mL of pyrrolidine was added and the reaction mixture was stirred overnight at room temperature. Then 9.6 mL of glacial acetic acid was added. The reaction mixture was stirred for one half hour and then the solvent was evaporated in a vacuum. The residue was dissolved in 200 mL of diethyl ether and washed five times with 100 mL of water. The organic phase was filtered using a silica gel and dried over sodium sulfate. The solvent was evaporated in a vacuum. A yellow oil was recovered which was identified as 6-(3-butenyl)-6-methylfulvene.

A solution was prepared by dissolving 10 g of fluorene in 100 mL of THF and

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then this was slowly reacted with 37.6 mL of a 1.6 molar solution of n-butyllithium in hexane. This dark red solution was stirred overnight at room temperature. Then a solution was prepared by combining 8.8 g of 6-(butenyl)-6-methylfulvene with 50 mL of THF. This latter solution was then added dropwise over a period of one half hour to the solution of the fluorenyl lithium salt. The resulting reaction mixture was stirred overnight at room temperature and then 100 mL of water was added. The organic phase was dried overnight over sodium sulfate and the solvent was evaporated in a vacuum. The yellow residue was dissolved in pentane and filtered using silica gel. The solvent was concentrated by means of evaporation. Crystallization took place at about -18°C to give 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene in the form of a white solid. This compound is also sometimes referred to as 1-(9-fluorenyl)-1-(cyclopentadienyl)-1-(but-3-enyl)-1-(methyl) methane.

#### Example II

Five grams of compound 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene was reacted with twice as many moles of n-butyllithium in 100 mL diethylether using conditions of the type taught in published European Patent Appln. No. 524,624 to produce the divalent ligand salt. The divalent ligand salt in diethyl ether was then reacted with 3.96 grams of zirconium tetrachloride at room temperature. The orange metallocene 1-(9-fluorenyl)-1-cyclopentadienyl)-1-(but-3-enyl)-1-(methyl) methane zirconium dichloride was recovered and purified by decanting off the liquid and recrystallization in dichloroethane at -18°C. Then the liquid was decanted off and the solid dried using a high vacuum.

#### Example III

The metallocene of Example II was employed to prepare solid prepolymerized

catalyst systems using two different techniques which differed in that in one the prepolymerization was begun at 0°C and in the other the prepolymerization was begun at 20°C. The catalyst preparations involved combining the metallocene and a toluene solution of methylaluminoxane. In another vessel, silica, specifically Davison 952 x 1836 Grade silica, was combined with the 10% methylaluminoxane and toluene; then the contents of the two vessels were combined. Then ethylene was added to the vessels and prepolymerization was carried out. The resulting prepolymerized solid catalyst system was then filtered and washed with toluene and hexane and then dried first using a membrane pump and then high vacuum. The resulting catalysts were then evaluated for their effectiveness in the polymerization of ethylene in a pilot plant scale continuous loop slurry reactor. The results of the pilot plant polymerizations are summarized in the following table.

TABLE I				
Run No.	Density, g/cc	MI, dg/min.	200 + pan wt%	Temp* °C
1	0.941	1.72	29.19	20
2	0.942	2.34	29.50	20
3	0.930	1.33	28.83	20
4	0.938	2.76	3.05	0
5	0.937	2.22	3.15	0
*Prepolymerization Temperature				

The above results demonstrate that when a catalyst is prepolymerized at the lower temperatures, the polymer ultimately produced using the catalyst contains significantly less polymer particles of dimensions which would be smaller than 200 mesh.

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**Example IV**

A prepolymerized solid catalyst system of the type disclosed in Example III was diluted with a polyethylene fluff having an MI of 18 dg/min and a density of 0.955 g/cc, a weight average molecular weight of 43,000 and a heterogeneity index of 3.03 produced  
5 using a catalyst such as disclosed in U.S. 4,326,988. The typical particle size analysis of such polymer is as follows:

20 mesh:2.43 weight percent  
40 mesh:40.04 weight percent  
60 mesh:36.98 weight percent  
100 mesh:14.06 weight percent  
200 mesh:4.89 weight percent  
pan:6.49 weight percent

Two techniques were tried for charging the mixture of the prepolymerized catalyst and polyethylene solid diluent to a continuous loop reactor using a mudpot and a ball  
15 check feeder.

One approach involved adding 990 gm of the solid prepolymerized catalyst with 0.5 liters of hexane and 0.8 ml of Stadis and then stirring into a slurry, then 380 gm of the polyethylene fluff in 0.5 liters of hexane was added and then the mixture stirred to form a slurry. This slurry was then charged to a transfer vessel using two 0.5 liter portions of  
20 hexane. In the continuous slurry polymerization process, periodically portions of that mixture was charged to the loop reactor via the check valve.

Another approach merely involved mixing the polyethylene fluff and the solid prepolymerized catalyst at a 2 to 1 weight ratio. That solid mixture was placed in the mudpot and then wetted with isobutane. Portions of the resulting mixture were then periodically

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charged into the continuous loop reactor via a ball check feeder.

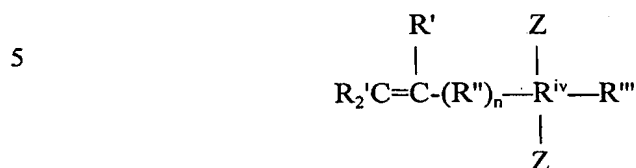
It was found that by using polyethylene as the particulate solid diluent it was possible to reduce or even eliminate the use of the antistatic agent. These catalyst diluent mixtures have been found to feed satisfactorily in a ball check feeder.

**THAT WHICH IS CLAIMED IS:**

1. A method for forming a solid particulate metallocene-containing catalyst system comprising (a) combining an organoaluminumoxane and at least one metallocene having at least one cyclopentadienyl-type ligand having at least one olefinic unsaturated substituent in a liquid to form a liquid catalyst system, (b) conducting prepolymerization of at least one  
 5 olefin in the presence of said liquid catalyst system to produce a prepolymerized solid catalyst, and (c) separating the resulting solid from the liquid and the components dissolved in the liquid, said solid being the solid particulate metallocene catalyst system, said method being further characterized by at least one of (1) by beginning at a temperature of less than 10°C and maintaining the prepolymerization temperature within the range of 3°C to 5°C of  
 10 the beginning temperature and (2) combining the prepolymerized solid catalyst with particulate polyethylene.

2. A method according to claim 2 wherein said prepolymerization of said at least one olefin is carried out in the presence of said liquid catalyst system at a beginning temperature of less than 10°C, to produce a prepolymerized solid catalyst.

3. A process according to claim 2, wherein step (a) is conducted in the presence of a bridged metallocene having olefinic unsaturation in a branch extending outwardly from the bridge, the ligand of said metallocene having the formula





wherein n is 1 or 0; R<sup>iv</sup> is Si, Ge, C, or Sn; each R' is individually selected from the group  
10 consisting of hydrogen and hydrocarbyl radicals having 1 to 10 carbons; R'' is selected from  
the group consisting of hydrocarbyl diradicals containing 1 to 10 carbons; R''' is selected  
from the group consisting of hydrogen or hydrocarbyl groups containing 1 to 10 carbons; and  
each Z is the same or different and is selected from the group consisting of substituted or  
unsubstituted cyclopentadienyl, indenyl, tetrahydroindenyl, and fluorenyl radicals.

4. A process according to claim 3, wherein the metallocene is selected  
from the group consisting of 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium  
dichloride, bis(9-fluorenyl)(methyl)(vinyl)silane zirconium dichloride, bis(9-  
fluorenyl)(methyl)(prop-2-enyl)silane zirconium dichloride, bis(9-fluorenyl)  
5 (methyl)(but-3-enyl)silane zirconium dichloride, bis(9-fluorenyl) (methyl) (hex-5-enyl)  
silane zirconium dichloride, bis(9-fluorenyl)(methyl)(oct-7-enyl)silane zirconium dichloride,  
(cyclopentadienyl)(1-allylindenyl) zirconium dichloride, bis(1-allylindenyl) zirconium  
dichloride, (9-(prop-2-enyl) fluorenyl)(cyclopentadienyl) zirconium dichloride,  
(9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl) zirconium dichloride, bis(9-  
10 (prop-2-enyl)fluorenyl) zirconium dichloride, (9-(cyclopent-  
2-enyl)fluorenyl)(cyclopentadienyl) zirconium dichloride, bis(9-(cyclopent-2-enyl)fluorenyl)  
zirconium dichloride, 5-(2-methylcyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium  
dichloride, 5-(fluorenyl)-5-(cyclopentadienyl)-1-hexene hafnium dichloride,  
(9-fluorenyl)(1-allylindenyl)dimethylsilane zirconium dichloride, 1-(2,7-di(alpha-  
15 methylvinyl)-(9-fluorenyl)-1-(cyclopentadienyl)-1,1-dimethylmethane zirconium dichloride,  
and 1-(2,7-di(cyclohex-1-enyl) 9-fluorenyl))-1-(cyclopentadienyl)-1,1-methane zirconium

dichloride.

- 5 5. A method according to claim 3 wherein the solid metallocene-containing catalyst system used in the polymerization is prepared by (a) combining 5-(9-fluorenyl)-5-(cyclopentadienyl)-hexene-1 zirconium dichloride and methylaluminumoxane in an aromatic liquid, (b) prepolymerizing ethylene in the resulting liquid, in the presence of silica, and (c) separating the resulting solid from the liquid.
6. A method according to claim 1 wherein the solid prepolymerized catalyst is combined with particulate polyethylene.
7. A method according to claim 6 wherein the weight ratio of the solid prepolymerized catalyst to the particulate polyethylene is about 2 to 1.
8. A process according to claim 7 wherein the particulate polyethylene is prepared using a titanium-containing catalyst.
9. A process according to claim 8 wherein the predominant particles of particulate polyethylene are those having sizes in the range of about 1 mm to 0.074 mm.
10. A process for polymerizing an olefin comprising contacting said olefin under suitable polymerization conditions with a solid metallocene-containing catalyst system produced by the process of claim 1.
11. A process according to claim 10 wherein the polymerization is conducted under slurry polymerization conditions.
12. A process according to claim 11 wherein ethylene is polymerized in the presence of an alkane liquid diluent.
13. A process according to claim 12 wherein said solid

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metallocene-containing catalyst system is prepared from 5-(9-fluorenyl)-5-(cyclopentadienyl)-hexene-1 zirconium dichloride.

14. A process according to claim 13 wherein the polymerization is conducted in a continuous loop reactor and isobutane is used as a liquid diluent for the polymerization.

15. A process according to claim 24 wherein the solid metallocene-containing catalyst system used in the polymerization is prepared by (a) combining 5-(9-fluorenyl)-5-(cyclopentadienyl)-hexene-1 zirconium dichloride and methylaluminoxane in a liquid, (b) prepolymerizing ethylene in the resulting liquid, in the presence of silica, and (c) separating the resulting solid from the liquid.

16. A process according to claim 15 wherein in the preparation of the prepolymerized catalyst system said prepolymerization of said at least one olefin is carried out in the presence of said liquid catalyst system at a beginning temperature of less than 10°C, to produce a prepolymerized solid catalyst.

17. A process according to claim 15 wherein the solid prepolymerized catalyst system is combined with particulate polyethylene.

18. A process according to claim 17 wherein a slurry of said prepolymerized catalyst system and said particulate polyethylene is placed in a settling vessel and periodically portions of the mixture are transferred to the polymerization vessel via a ball check valve.

**AMENDED CLAIMS**

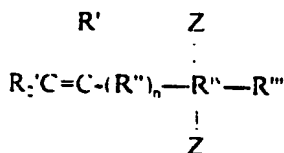
[received by the International Bureau on 17 March 1998 (17.03.98);  
original claims 2 and 15 amended; remaining claims unchanged (2 pages)]

**THAT WHICH IS CLAIMED IS:**

1. A method for forming a solid particulate metallocene-containing catalyst system comprising (a) combining an organoaluminoxane and at least one metallocene having at least one cyclopentadienyl-type ligand having at least one olefinic unsaturated substituent in a liquid to form a liquid catalyst system. (b) conducting prepolymerization of at least one olefin in the presence of said liquid catalyst system to produce a prepolymerized solid catalyst. and (c) separating the resulting solid from the liquid and the components dissolved in the liquid. said solid being the solid particulate metallocene catalyst system. said method being further characterized by at least one of (1) by beginning at a temperature of less than 10°C and maintaining the prepolymerization temperature within the range of 3°C to 5°C of the beginning temperature and (2) combining the prepolymerized solid catalyst with particulate polyethylene.

2. A method according to claim 1 wherein said prepolymerization of said at least one olefin is carried out in the presence of said liquid catalyst system at a beginning temperature of less than 10°C. to produce a prepolymerized solid catalyst.

3. A process according to claim 2. wherein step (a) is conducted in the presence of a bridged metallocene having olefinic unsaturation in a branch extending outwardly from the bridge. the ligand of said metallocene having the formula



metallocene-containing catalyst system is prepared from 5-(9-fluorenyl)-5-(cyclopentadienyl)-hexene-1 zirconium dichloride.

14. A process according to claim 13 wherein the polymerization is conducted in a continuous loop reactor and isobutane is used as a liquid diluent for the polymerization.

15. A process according to claim 14 wherein the solid metallocene-containing catalyst system used in the polymerization is prepared by (a) combining 5-(9-fluorenyl)-5-(cyclopentadienyl)-hexene-1 zirconium dichloride and methylaluminoxane in a liquid, (b) prepolymerizing ethylene in the resulting liquid, in the presence of silica, and (c) separating the resulting solid from the liquid.

16. A process according to claim 15 wherein in the preparation of the prepolymerized catalyst system said prepolymerization of said at least one olefin is carried out in the presence of said liquid catalyst system at a beginning temperature of less than 10°C. to produce a prepolymerized solid catalyst.

17. A process according to claim 15 wherein the solid prepolymerized catalyst system is combined with particulate polyethylene.

18. A process according to claim 17 wherein a slurry of said prepolymerized catalyst system and said particulate polyethylene is placed in a settling vessel and periodically portions of the mixture are transferred to the polymerization vessel via a ball check valve.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/08862

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>																						
IPC(6) : B01J 31/00, 37/00; C08F 4/02, 4/60, 4/44, 2/00; C08G 85/00 US CL : 502/103, 104, 109, 117; 526/64, 160, 904, 943 According to International Patent Classification (IPC) or to both national classification and IPC																						
<b>B. FIELDS SEARCHED</b>																						
Minimum documentation searched (classification system followed by classification symbols) U.S. : 502/103, 104, 109, 117; 526/64, 160, 904, 943																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																						
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X	US 5,498,581 A (WELCH ET AL) 12 March 1996 (12/03/96), see entire document, especially column 1, line 15-23, 47-50, 61-68; column 2, line 1-14; column 3, line 55-56; column 4, line 63-67; column 5, line 1-9; column 6, line 31-41; column 7, line 9-19, line 62-67; column 8, line 1-6.	1, 6-14																				
A	US 5,283,300 A (HASPESLAGH ET AL) 01 February 1994 (01/02/94).	1, 6-14																				
A	US 5,466,766 A (PATSIDIS ET AL) 14 November 1995 (14/11/95).	1, 6-14																				
A	US 5,449,651 A (REDDY ET AL) 12 September 1995 (12/09/95).	1, 6-14																				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																						
<table border="0"> <tr> <td>* "A"</td> <td>Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>* "E"</td> <td>earlier document published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>* "L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>* "O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"Z"</td> <td>document member of the same patent family</td> </tr> <tr> <td>* "P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	* "E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	* "L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	* "O"	document referring to an oral disclosure, use, exhibition or other means	"Z"	document member of the same patent family	* "P"	document published prior to the international filing date but later than the priority date claimed		
* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																			
* "E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																			
* "L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
* "O"	document referring to an oral disclosure, use, exhibition or other means	"Z"	document member of the same patent family																			
* "P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 17 JULY 1997		Date of mailing of the international search report 24 SEP 1997																				
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JAMES PASTERCZYK Telephone No. (703) 308-0661																				

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/08862

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,262,498 A (ANTBERG ET AL) 16 November 1993 (16/11/93).	1, 6-14

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/08862

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 2-5 and 15-18  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
  
Claim 2 depends from itself; claims 3-5 ultimately depend from claim 2. Claim 15 depends from a nonexistent claim; claims 16-18 ultimately depend from claim 15.
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.